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COMPLETE SPECIFICATION Ionic Hydrocarbon Polymers

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 10th and Market Street, Wilmington, Delaware, United States of America, (Assignee of RICHARD WATKIN REES), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to novel hydrocarbon polymers, and, more particularly, to hydrocarbon polymers which contain ionic crosslinks.

The crosslinking of hydrocarbon polymers is well known in the art. Thus, polymeric hydrocarbon elastomer, such as natural rubber, are crosslinked or vulcanized by the use of sulfur, which reacts with the carbon of the unsaturated bonds in polymer molecules to form a bridge between two molecules so that one polymer molecule is covalently bonded to a second polymer molecule. If sufficient crosslinks of this type occur in the polymeric hydrocarbon, all molecules are joined in a single giant molecule. The characteristic property of a crosslinked polymer is its intractability above the softening point or melting point normally observed in the uncrosslinked base polymer. Thus, whereas the uncrosslinked polymer has a marked softening point or melting point above which the polymer is fluid and deformable, the crosslinked polymer retains its shape and will tend to return that shape when deformed at all temperatures at which the polymer is stable and can not be permanently deformed. Although once crosslinked the polymer is no longer fabricable, except possibly by machining, crosslinked polymers have found wide utility because of the significant improvement in the physical properties obtained by crosslinking. Thus, by vulcanizing rubber elasti-

city, impact resistance, flexibility, thermal stability and many other properties are either introduced or improved. The crosslinking of non-elastomeric polymers increases the toughness, abrasion resistance and, particularly, the upper use temperatures of the material.

In addition to the vulcanization of diene hydrocarbon polymers using sulfur, other methods of crosslinking hydrocarbon polymers which do not require a double bond and which do not use sulfur have been developed. Thus, saturated hydrocarbon polymers and, in particular, polyethylene, are cross-linked by reactions resulting from the addition of a peroxide to the polymer at elevated temperatures. Peroxides decompose to form free radicals which in turn attack the polymer chain to form crosslinking sites which then react to form crosslinks. Irradiation of polyethylene also results in a crosslinked product by substantially the same mechanism except that the free radicals are generated by decompositon of the polymer itself. By either method, however, a product is obtained which is intractable and cannot be further fabricated by techniques normally used in the fabrication of polyethylene, such as melt extrusion or injection molding. The improvement obtained in the solid state properties of a hydrocarbon polymer by crosslinking have, therefore, been always combined with a loss in fabricability as a result of which crosslinked hydrocarbon polymers, with the exception of elastomeric hydrocarbon polymers, have found little commercial success as compared to the uncrosslinked hydrocarbon polymers. Furthermore, crosslinking reduces the crystallinity of saturated hydrocarbon polymers, thereby decreasing the stiffness and rigidity of the product.

It is an object of the present invention to provide a new class of hydrocarbon polymers. It is a further object of the present invention to provide a new class of hydrocarbon poly-

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mers of greatly improved solid state properties. It is a further object to provide hydrocarbon polymers which combine desirable solid state properties of crosslinked hydrocarbon polymers with melt flow properties of uncrosslinked hydrocarbon polymers.

According to the present invention there is provided a copolymer characterized by having ionic crosslinks in the solid state, which crosslinks are removable on fusion of the copolymer and restored on its reversion to the solid state, which comprises ethylene, and an α,β -ethylenically unsaturated mono- or di-carboxylic acid, the ethylene content being at least 50 mol percent based on the polymer and the acid monomer content being from 0.2 to 25 mol percent based on the polymer, the copolymer having a melt index of 0.1 to 100 g/10 minutes in the absence of metal ions and wherein at least 10% of the carboxylic acid groups are neutralized by one or more metal ions having a valence of 1 to 3 inclusive wherein the acid monomer is monocarboxylic, and a valence of 1 where the acid monomer is dicarboxylic.

25 The concentration of the ethylene is at least 50 mol percent in the copolymer, and is preferably greater than 80 mol percent.

The α,β -ethylenically unsaturated carboxylic acid group containing monomer preferably has from 3 to 8 carbon atoms. Examples of such monomers are acrylic acid, methacrylic acid, ethacrylic acid, itaconic acid, maleic acid, fumaric acid, monoesters of said dicarboxylic acids, such as methyl hydrogen maleate, methyl hydrogen fumarate, ethyl hydrogen fumarate and maleic anhydride. Although maleic anhydride is not a carboxylic acid in that it has no hydrogen attached to the carboxyl groups, it can be considered an acid 40 for the purposes of the present invention because of its chemical reactivity being that of an acid. Similarly, other α,β -monoethylenically unsaturated anhydrides of carboxylic acids can be employed. As indicated above, the 45 concentration of acidic monomer in the copolymer is from 0.2 mol percent to 25 mol percent, and, preferably, from 1 to 10 mol percent.

The base copolymers employed in forming the ionic copolymers of the present invention 50 are prepared by the direct copolymerization of a mixture of ethylene and the carboxylic acid monomer. Methods employed for the preparation of ethylene carboxylic acid copolymers have been described in the literature. In a 55 preferred process, a mixture of the two monomers is introduced into a polymerization environment maintained at high pressures, 50 to 3000 atmospheres, and elevated temperatures, 150 to 300° C, together with a free 60 radical polymerization initiator such as a peroxide. An inert solvent for the system, such as water or benzene, may be employed, or the polymerization may be substantially a bulk polymerization.

65 The copolymers employed to form ionic

copolymers which are useful as plastics are preferably of high molecular weight in order to achieve the outstanding combination of solid state properties of crosslinked polyolefins with the melt fabricability of uncrosslinked polyolefins. Although the mechanical properties of a low molecular weight copolymer are improved by the process of the present invention, the resulting product does not exhibit such mechanical properties as are markedly superior to the same unmodified copolymer when of high molecular weight. The molecular weight of the copolymers useful as base resins is most suitably defined by melt index, a measure of melt viscosity, described in detail in ASTM—D—1238—57T. The melt index of copolymers employed in the formation of ionic copolymers which are useful as plastics is in the range of 0.1 to 100 g/10 min, and, particularly, in the range of 1.0 to 20 g/10 min. However, it should be pointed out that low molecular weight copolymers result in ionic copolymers which, although not suitable as plastics, are outstanding adhesives and laminating resins.

The copolymer base need not necessarily comprise a two component polymer. Thus, although the ethylene content of the copolymer should be at least 50 mol percent, more than one olefin can be employed to provide the hydrocarbon nature of the copolymer base. Additionally, any third copolymerizable monomer can be employed in combination with the olefin and the carboxylic acid comonomer. The scope of base copolymers suitable for use in the present invention is illustrated by the following examples: Ethylene/acrylic acid copolymers, ethylene/methacrylic acid copolymers, ethylene/itaconic acid copolymers, ethylene/methyl hydrogen maleate copolymers, ethylene/maleic acid copolymers, ethylene/acrylic acid/methyl methacrylate copolymers, ethylene/methacrylic acid/ethyl acrylate copolymers, ethylene/itaconic acid/methyl methacrylate copolymers, ethylene/methyl hydrogen maleate/ethyl acrylate copolymers, ethylene/vinyl acetate copolymers, ethylene/acrylic acid/vinyl alcohol copolymers, ethylene/propylene/acrylic acid copolymers, ethylene/styrene/acrylic acid copolymers, ethylene/methacrylic acid/acrylonitrile copolymers, ethylene/fumaric acid/vinyl methyl ether copolymers, ethylene/vinyl chloride/acrylic acid copolymers, ethylene/vinylidene chloride/acrylic acid copolymers, ethylene/vinyl fluoride/methacrylic acid copolymers, and ethylene/chlorotrifluoroethylene/methacrylic acid copolymers.

The copolymers may also, after polymerization but prior to ionic crosslinking, be further modified by various reactions to result in 125 polymer modifications which do not interfere with the ionic crosslinking. Halogenation of an ethylene-acid copolymer is an example of such polymer modification.

The preferred base copolymers, however, are 130

those obtained by the direct copolymerization of ethylene with a monocarboxylic acid comonomer in the absence or presence of a third copolymerizable monoethylenically unsaturated monomer.

The ionic copolymers of the present invention are obtained by the reaction of the described copolymer base with an ionizable metal compound. This reaction is referred to herein as "neutralization". The reaction mechanism involved in the formation of the ionic copolymers and the exact structure of the copolymers are at the present time not completely understood. However, a comparison of the infrared spectrum of the copolymer base with that of the ionic copolymer shows the appearance of an absorption band at about 6.4 micron which is characteristic of the ionized carboxyl group, COO^- , a decrease in the crystallinity band at 13.7 micron and a substantial decrease, depending on the degree of neutralization, of a band at 10.6 micron, characteristic of the unionized carboxyl group, COOH . It is consequently deduced that the surprising properties of ionic copolymers are the result of an ionic attraction between the metal ion and one or more ionized carboxylic acid groups.

This ionic attraction results in a form of crosslinking which occurs in the solid state. However, when molten and subjected to the shear stresses which occur during melt fabrication, the ionic crosslinks of these polymers are ruptured and the polymers exhibit melt flow essentially the same as that of the linear base copolymer. On cooling of the melt and in the absence of the shear stress occurring during fabrication, the crosslinks, because of their ionic nature, are reformed, and the solidified copolymer again exhibits the properties of a crosslinked material.

The change in properties resulting from the neutralization of the base copolymer to the ionic copolymer is greatly influenced by the degree of neutralization and, therefore, the number of ionic crosslinks and the nature of the crosslinks involved. Although an improvement in solid state properties is obtained with even a small percentage of the acid groups neutralized, in general, a noticeable improvement is observed only after 10 percent of the acid groups have been neutralized. However, to obtain the optimum solid state properties which are derivable from ionic copolymers, the number of crosslinks should be sufficient to form an infinite network of crosslinked polymer chains. This, of course, not only depends on the degree of neutralization, but also on the number of crosslinking sites and the molecular weight of the base copolymer. In general, it was found that base copolymers having molecular weights as measured by melt index of 1 to 5 g/10 min and a monocarboxylic acid concentration of 5 to 10 percent show optimum solid state properties upon 50 to 80 percent neutralization. The degree of neutralization can be decreased as the molecular weight of the copolymer base is increased or as the acid content of the copolymer base is increased without significantly changing the solid state properties. In general, no substantial further improvement in solid state properties is observed if the crosslinking is continued beyond the point at which an infinite network is formed. However, the shear stress necessary to break the ionic crosslink and, thus, make the copolymer melt fabricable is steadily increased with an increasing number of crosslinks beyond that necessary to achieve an infinite network.

The melt fabricability of the ionic copolymer is affected not only by the number of crosslinks, but to a much greater degree, is affected by the nature of the crosslink. Thus, it was found that the combination of certain types of acids result in intractible materials which do not lend themselves to melt fabrication. Thus, it was found that base copolymers with dicarboxylic acid comonomers, even those in which one acid radical has been esterified, when neutralized with metal ions which are di- or higher valent, result in intractible ionic copolymers at the level of neutralization essential to obtain significant improvement in solid state properties. Similarly, base copolymers with monocarboxylic acid comonomers result in intractible ionic copolymers when neutralized with tetravalent metal ions to the indicated degree. It is believed that the nature of the ionic bond in these instances is too strong to be suitable for the formation of ionic copolymers which exhibit solid state properties of crosslinked resins and melt properties of uncrosslinked resins.

The metal ions which are suitable in forming the ionic copolymers of the present invention, therefore, comprise for the ethylene-monocarboxylic acid copolymers, mono-, di- and trivalent metal ions. In particular, the mono-, di- and trivalent ions of metals in Groups I, II, III, IV-A and VIII of the Periodic Table of Elements (see page 392, Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, 37th Edition) are suitable crosslinking metal ions. Monovalent metal ions of the metals in the stated groups are also suitable in forming the ionic copolymers of the present invention with copolymers of ethylene and ethylenically unsaturated dicarboxylic acids. Suitable monovalent metal ions are Na^+ , K^+ , Yi^+ , Cs^+ , Ag^+ , Hg^+ and Cu^+ . Suitable divalent metal ions are Be^{+2} , Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Cu^{+2} , Cd^{+2} , Hg^{+2} , Sn^{+2} , Pb^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} and Zn^{+2} . Suitable trivalent metal ions are Al^{+3} , Sc^{+3} , Fe^{+3} and Y^{+3} .

The preferred metals, regardless of the nature of the copolymer base are the alkali metals. These metals are preferred because they result in ionic copolymers having the best combination of improvement in solid state

properties with retention of melt fabricability. It is not essential that only one metal ion be employed in the formation of the ionic copolymers and more than one metal ion may be preferred in certain applications.

The quantity of ions employed or the degree of neutralization will differ with the degree of solid property change and the degree of melt property change desired. In general, it was found that the concentration of the metal ion should be at least such that the metal ion neutralizes at least 10 percent of the carboxylic acid groups in order to obtain a significant change in properties. As explained above, the degree of neutralization for optimum properties will vary with the acid concentration and the molecular weight of the copolymer. However, it is generally desirable to neutralize at least 50 percent of the acid groups. The degree of neutralization may be measured by several techniques. Thus, infrared analysis may be employed and the degree of neutralization calculated from the changes resulting in the absorption bands. Another method comprises the titration of a solution of the ionic copolymer with a strong base. In general, it was found that the added metal ion reacts stoichiometrically with the carboxylic acid in the polymer up to 90 percent neutralization. Small excess quantities of the crosslinking agent are necessary to carry the neutralization to completion. However, large excess quantities of the crosslinking agent do not add to the properties of the ionic copolymer of the present invention since once all carboxylic acid groups have been ionically crosslinked, no further crosslinks are formed.

The crosslinking of the ionic copolymer is carried out by the addition of a metal compound to the base copolymer. The metal compound which is employed must contain the metal in the ionic state rather than covalently bonded. The crosslinking compound employed is generally water soluble. A compound is considered water-soluble for the purposes of the present invention if it is soluble in water at room temperature to the extent of two weight percent. This requirement is explained as separating those ionic compounds which are capable of exchanging a metal ion for the hydrogen ion of the carboxylic acid group in the copolymer from those which do not interact with the acid. The third requirement for the metal compound employed to give rise to the ionic crosslink is that the salt radical reacting with the hydrogen of the carboxylic acid group must form a compound which is removable from the copolymer at the reaction conditions. This requirement is essential to obtain the carboxylic acid group of the copolymer in ionic form and, furthermore, to remove the salt radical from the copolymer so that the attraction between the ionized carboxylic acid groups of the copolymer and the metal ion is not overshadowed by the attraction of the metal

ion and its original salt radical. Although the foregoing limits delineate metal compounds suitable in forming metal ions in the acid copolymers which result in ionic crosslinks, certain types of compounds are preferred because of their ready availability and ease of reaction. Preferred metal salts include formates, acetates, hydroxides of sufficient solubility, methoxides, ethoxides, nitrates, carbonates and bicarbonates. Metal compounds which are generally not suitable in resulting in ionic crosslinks include in particular metal oxides because of their lack of solubility, metal salts of fatty acids which form non-volatile residues remaining in the polymer and metal coordination compounds which lack the necessary ionic character.

The crosslinking reaction is carried out under conditions which allow for a homogeneous distribution of the crosslinking agent in the copolymer base. No particular reaction conditions are essential except that the conditions should permit the volatilization of the hydrogen-salt radical reaction product. Since the homogeneous distribution of the crosslinking agent and the necessary volatilization of the hydrogen-salt radical reaction product is difficult at room temperature, elevated temperatures are generally employed. More specifically, the crosslinking reaction is carried out either by melt blending the polymer with the crosslinking metal compound, which preferably is employed in solution, or by adding the crosslinking agent, directly or in solution, to a solution of the copolymer base and then, on reaction, precipitating and separating the resulting polymer. Of these techniques, the first is greatly preferred because of its relative simplicity. It is to be understood, however, that the specific technique employed is not critical as long as it meets the specific requirements set forth above.

The following examples further illustrate the methods employed in forming the ionic copolymers of the present invention.

EXAMPLE I

A 500 g sample of an ethylene/methacrylic acid copolymer, containing 10 weight percent of methacrylic acid and having a melt index of 5.8 g/10 min (ASTM-D-1238-57T) was banded on a six inch rubber mill at 50° C. After the copolymer had attained the mill temperature, 24 g of sodium methoxide dissolved in 100 ml of methanol was added to the copolymer over a period of five minutes as working of the copolymer on the mill was continued. Melt blending of the composition was continued for an additional 15 minutes during which time the initially soft, fluid melt became stiff and rubbery on the mill. However, the polymer could still be readily handled on the mill. The resulting product was found to have a melt index of less than 0.1 g/10 minutes and resulted in transparent, as compared to opaque for the copolymer base, moldings of greatly improved tensile properties.

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EXAMPLE II

5 To a solution of 50 g of an ethylene/methacrylic acid copolymer containing 10 weight percent of methacrylic acid and having a melt index of 5.8 g/10 minutes in 250 ml of xylene maintained at a temperature of 100° C was added three g of strontium hydroxide dissolved in 50 ml of water. Gelation followed immediately. The product was recovered by precipitation with methanol and washed thoroughly with water and acetone. The final dry product was found to have a melt index of 0.19 g/10 minutes and resulted in glass clear moldings.

EXAMPLE III

15 To 50 g of an ethylene/methacrylic acid copolymer containing 10 weight percent of methacrylic acid and having a melt index of 5.8 g/10 minutes milled at a temperature of 125 to 135° C on a 6 inch rubber mill was added gradually 6.3 g of magnesium acetate ($\times 4H_2O$) in 25 ml of water. Milling was continued for 15 minutes at which time the evolution of acetic acid had ceased. The product had a melt index of 0.12 g/10 minutes and resulted in clear, resilient moldings.

EXAMPLE IV

30 To 50 g of an ethylene/itaconic acid copolymer having a melt index of 9 g/10 minutes and containing three percent by weight of the copolymer of itaconic acid was gradually added three g of sodium hydroxide in 20 ml of water while the polymer was being worked

on a six inch rubber mill at a temperature of 150° C. Upon addition of the hydroxide, the polymer melt became stiff, transparent and elastomeric.

EXAMPLE V

35 An ethylene/methacrylic acid copolymer containing 10 percent methacrylic acid was banded on a two roll mill at 170° C and 3.6 weight percent of powdered sodium hydroxide was added over a period of two minutes. Milling was continued over a period of 10 minutes to ensure homogeneity. The ionic copolymer obtained was reduced more than ten-fold in melt index and was glass clear and resilient. When extruded as a melt, the ionic copolymer could be drawn into fibers having pronounced elastic recovery.

40 Specific examples of the ionic copolymers of the present invention and their properties are shown in the following tables.

45 Table I shows physical properties of ionic copolymers obtained from an ethylene/methacrylic acid copolymer with monovalent, divalent and trivalent metal ions. The ethylene/methacrylic acid copolymer employed contained 10 weight percent of the acid and had a melt index of 5.8 g/10 minutes. In addition to the improvements shown in the table, all these 50 ionic copolymers exhibited excellent bend recovery which was not exhibited by the copolymer base. The tests were carried out on compression molded sheets of the ionic copolymer.

TABLE I

Metal Cation	—	Na ⁺	Li ⁺	Sr ⁺⁺	Mg ⁺⁺	Zn ⁺⁺	Al ⁺⁺
Metal Anion	—	CH ₃ O ⁻	OH ⁻	CH ₃ COO ⁻			
Wt. % of Cross-linking Agent	—	4.8	2.8	9.6	8.4	12.8	14
Melt Index g/10 min.	5.8	0.03	0.12	0.19	0.12	0.09	0.25
Yield Point* in psi	890	1920	1906	1954	2176	1926	1035
Elongation* in %	553	330	317	370	326	313	347
Ult. Tens. St.* in psi	3,400	5200	4920	4900	5862	4315	3200
Stiffness** in psi	10,000	27,600	30,000	32,400	23,800	30,170	15,000
Transparency (visual)	Hazy	Clear	Clear	Clear	Clear	Clear	Clear

* ASTM D-412—51T

** ASTM D-747—58T

Table II shows the effect of varying concentrations of crosslinking agent and varying concentrations of carboxylic acid groups on the solid state properties of an ethylene methacrylic acid copolymer employing sodium methoxide as the crosslinking agent. 5

TABLE II

	5	10	70% of Stoichiom.	90% of Stoichiom.	10	Stoichiom.	10	in excess of Stoichiom.	16	in excess of Stoichiom.
% Methacrylic Acid	5	5	5.8	5.8	5.8	5.8	5.8	5.8	25	0.01
% Sodium Added	in excess of Stoichiom.	in excess of Stoichiom.	0.09	0.05	0.02	0.01	0.01	0.01	0.01	0.01
Copolymer Base Melt Index in g/10 min.	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Melt Index of Crosslinked Polymer in g/10 min.	1300	1924	1900	1900	1900	1900	1900	1900	1900	1900
Yield Point* in psi	273	330	3 00	340	340	340	340	340	340	340
Elongation*	3550	5200	4200	5000	5000	5000	5000	5000	5000	5000
Ult. Tens. Str.* in psi	14,200	27,600	26,200	27,200	27,200	27,200	27,200	27,200	27,200	27,200
Stiffness*** in psi]	Slight Haze	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Transparency										

* ASTM—D—412—51T

** ASTM—D—747—58T

Table III illustrates the ionic crosslinking of copolymers than with low molecular weight ethylene/dicarboxylic acid copolymers, although with both a significant sodium acetate as the crosslinking agent. The decrease of melt flow is obtained in the melt indexer. The table also illustrates that the crosslinking is 5 more effective with high molecular weight

TABLE III

Copolymer	% Sodium Hydroxide	Melt Index in g/10 min.	Yield Strength* in psi.	Ult. Tens. Strength in psi.	Elongation in %*	Stiffness* in psi.	Transparency
Ethylene/3 wt. % maleic anhydride copolymer	—	1000	1185	1180	200	18000	Opaque
Ethylene/3 wt. % maleic anhydride copolymer	1.2	0.1	1300	2100	290	17400	Hazy
Ethylene/2—3 wt. % methyl hydrogen maleate copolymer	—	6.8	1250	2000	520	19000	Opaque
Ethylene/2—3 wt. % methyl hydrogen maleate copolymer	1.8	0.1	1350	3100	380	23500	Hazy
Ethylene/2—3 wt. % methyl hydrogen maleate copolymer	—	44.5	1420	1800	450	24600	Opaque
Ethylene/2—3 wt. % maleic acid copolymer	6	No flow	1440	3000	260	17000	Hazy
Ethylene/2—3 wt. % maleic acid copolymer	—	9.0	1320	1800	433	15800	Opaque
Ethylene/6 wt. % itaconic acid copolymer	—	0.11	1528	1900	180	30000	Hazy
Ethylene/6 wt. % itaconic acid copolymer	2.0						

* ASTM—D—412—51T
** ASTM—D—747—58T

Table IV shows the surprising melt properties of the ionic copolymers. The ionic copolymers illustrated were obtained by reacting aqueous or methanolic solutions of the crosslinking agents indicated in the table with the copolymers indicated on a two roll mill at temperatures of 150 to 200° C until homogeneous compositions were obtained. In each instance sufficient quantities of the crosslinking agent were added to neutralize all of the acid groups. The melt index of the copolymer base and the ionic copolymer are compared and contrasted against the flow number which corresponds to the melt index, except that a temperature of 250° C and a weight of 5000 g is employed. Polyethylene which is crosslinked by peroxides or by ionizing radiation shows no flow for the conditions employed to measure the flow number. As can be seen from the table, at low shear stresses, i.e., under conditions at which melt index is measured, the ionic copolymers have low melt indices as compared to the base copolymers. However, at higher temperatures and under higher shear stresses the ionic copolymers show greatly improved flow.

Table IV further illustrates some of the requirements which must be met to obtain the ionic copolymers of the present invention. Thus, the use of zinc metal (Product No. 7) which is not ionized, does not result in any

ionic crosslinking. Zinc oxide, which is ionic when dissolved in water and when employed as a crosslinking agent (Product No. 8), results in only a partial ionic copolymer because zinc oxide does not dissolve sufficiently in water or other polar solvents. Zinc stearate is not effective as a crosslinking agent (Product No. 9) to give rise to an ionic copolymer because the stearate radical remains in the polymer. As can be seen from the combination of a monocarboxylic acid with a trivalent metal (Product No. 6) a borderline improvement in the melt flow properties is obtained at higher shear stresses which is explained by the greater ionic attraction between the metal ion in a higher valence state and the carboxylic acid group. The inoperability of divalent metal ions and dicarboxylic acid groups (Products 21 and 17) to result in ionic copolymers of the present invention is also illustrated. These polymers are believed to have such strong ionic bonds that they in effect act like regularly crosslinked polyolefins. The table further illustrates the wide variety of metal ions which are suitable crosslinking agents. Additionally, the table also shows that the presence of a third monomer does not interfere in the formation of the ionic copolymers of the present invention.

TABLE IV

Product No.	Comonomer(s)	Comonomer Conc.	Crosslinking Reagent	Copolymer Base M.I. g/10 min.	Ionic Copolymer MI in g/10 min.	Flow Number in g/10 min.
1	Methacrylic Acid	10.0	Sodium hydroxide	6.3	0.03	4.9
2	Methacrylic Acid	10.0	Sodium hydroxide	5.8	No flow	5.5
3	Methacrylic Acid	10.0	Lithium hydroxide	5.8	0.12	6.5
4	Methacrylic Acid	10.0	Zinc Acetate	5.8	0.13	7.0
5	Methacrylic Acid	10.0	Magnesium acetate	5.8	0.107	6.5
6	Methacrylic Acid	10.0	Aluminum hydroxide	5.8	0.2	0.5
7	Methacrylic Acid	10.0	Zinc Metal	5.8	6.5	—
8	Methacrylic acid	10.0	Zinc Oxide	5.8	0.98	—
9	Methacrylic Acid	10.0	Zinc Stearate	5.8	4.8	—
10	Methacrylic Acid	10.0	Nickel acetate	5.8	0.25	—
11	Methacrylic Acid	10.0	Cobalt Acetate	5.8	0.13	—
12	Methacrylic Acid	10.0	Sodium Carbonate	5.8	0.05	—
13	Methacrylic Acid	10.0	Tin Acetate	5.8	0.17	—
14	Methacrylic Acid	10.0	Sodium Methoxide	5.8	0.03	—
15	Methacrylic Acid	10.0	Sodium Formate	5.8	0.08	—
16	Itaconic Acid	6	Sodium Hydroxide	9.0	0.11	0.8
17	Itaconic Acid	6	Strontium hydroxide	9.0	No flow	No flow
18	Itaconic Acid	6	Zinc Oxide	9.0	No flow	1.2
19	Maleic Anhydride	3	Sodium hydroxide	300	0.008	1.66
20	Maleic Anhydride	3	Lithium hydroxide	300	No flow	No flow
21	Maleic Anhydride	3	Zinc Acetate	300	0.45	7.2
22	Vinyl Acetate + Methacrylic Acid	15	Sodium hydroxide	5.5	Magnesium Acetate	5.8
23	Vinyl Acetate + Methacrylic Acid	15	Magnesium Acetate	5.5	0.12	5.8
24	Methyl Methacrylate / Methacrylic Acid	15	Sodium Hydroxide	3.6	0.16	6.2
25	Styrene/Methacrylic Acid	15	Sodium Hydroxide	6.0	0.13	7.5

EXAMPLE VI

5 An ethylene/methacrylic acid copolymer containing 10 percent of methacrylic acid was ionically crosslinked with sodium hydroxide until 76 percent of the carboxyl groups had been neutralized. The melt index of the resulting polymer was 0.65 g/10 minutes. This resin was extruded through a one inch extruder equipped with a tubular film die and take-off.

10 The ionic copolymer was extruded into 0.5 mil film using a 225° C temperature for the extruder barrel and a 250° C temperature for the die. The resulting film was completely haze-free and transparent. Dart drop test gave

15 a value of 375 g at 0.5 mil thickness. Comparable values for polyethylene ($\rho=0.92\text{g/cc}$) are 50 g. Pneumatic impact was 7.4 kg-cm/mil; a polyterephthalate ester film has a value of 6.5 kg-cm/mil. In addition to its excellent impact resistance, this film displayed marked shrinkage when immersed in boiling water making it ideal for many packaging applications. X-ray examination showed the film to be biaxially oriented.

EXAMPLE VII

25 Using the ionic copolymer of Example VII, a 30 mil wire coating was produced on #14 copper wire. A three and one-quarter inch Davis-Standard wire coater fitted with an 0.124 inch tapered pressure die was employed. Extrusion was carried out at 450 ft/minute using temperature settings of 457° F on the barrel and 490° F on the die and quench temperatures of 200° F to 72° F. A very smooth, glassy, coating was obtained displaying excellent toughness and electrical properties. Polyethylene having the same melt index could not be extruded into a continuous smooth wire coating under these conditions.

EXAMPLE VIII

40 Using the ionic copolymer of Example VII injection molded combs, chain links, gears, coil forms and chips were made. A one fluid ounce machine fitted with a 7/8 inch cylinder was employed. The machine was operated at a cylinder temperature of 225° C and a mold temperature of 55° C. Pressures ranging from 3000 to 6000 psi and a 30/30 second cycle were found to be adequate. The moldings were tough and transparent and reproduced the finest details of the molds employed. Polyethylene of the same melt index did not fill the molds under these conditions.

EXAMPLE IX

55 Using the ionic copolymer of Example VII, four ounce Boston Round bottles were prepared. The resin was extruded through a two inch extruder fitted with a cross-head tubing die (O.D. 11/16 inch, I.D. 1/2 inch) and 60 blown into a bottle using a 4 ounce Boston Round bottle mold. The resin was heated to 175° C in the extruder. The extrusion screw speed was 25 rpm. The bottles obtained were stiff, transparent and directly printable.

65 The foregoing examples and experimental

70 data have demonstrated the surprising combination of improvement in solid state properties and retention of melt properties obtained by the compositions of the present invention. One of the more apparent improvements obtained is that of transparency. Hydrocarbon polymers are generally not transparent in all but exceptionally thin forms and even there special techniques such as quenching and drawing must be employed to obtain a measure of transparency. The copolymers of the present invention, however, can be made to be transparent even in thick molded sections. Another solid state property which is markedly improved by ionic crosslinking is the resilience or bend recovery of the copolymer. In contrast to hydrocarbon polymers which have a slow and incomplete recovery from bend, the copolymers of the present invention snap back when deformed and assume their original shape. The improvement obtained in tensile properties and stiffness is apparent from the data presented in the tables. In this respect the copolymers of the present invention exhibit greatly surprising properties. In contrast to peroxide-crosslinked polyethylene where the stiffness is decreased by crosslinking, the ionic copolymers exhibit even greater stiffness and rigidity than the unmodified base polymer. Other solid state properties improved by ionic crosslinking are toughness and stress-crack resistance. The impact strength of thin films made from ionic copolymers is equal to and better than that of polyterephthalate films which are considered the toughest plastic films commercially available. Tests designed to measure stress-crack resistance of hydrocarbon polymers using detergents commonly used in such tests failed to result in failures and, thus, the ionic copolymers are considered to be free from stress-cracking.

75 The ionic copolymers of the present invention also exhibit highly surprising rheological properties. Thus, although having extremely low melt indices, which would indicate that the 80 ionic copolymers are not melt fabricable, the opposite is true in that the ionic copolymers can be melt extruded, injection molded and compression molded with ease. This is explained, of course, by the difference in shear stress exerted on the melt in a melt indexer and in an extruder, for example. At low shear stresses the high melt strength of the polymer results in low melt flow. However, once this is 85 overcome by a higher shear stress, the ionic copolymer flow readily. The combination of high melt strength at low shear stresses and good melt flow at high shear stresses is highly desirable in all applications requiring forming of the melt subsequent to extrusion such as in 90 bottle blowing in which an extruded parison is 95 blown into a bottle and in thermoforming in which molten sheet is forced against a mold by means of a vacuum. In both these fabrication 100 techniques, the polymer melt becomes unsup- 105

ported during some part of the fabrication cycle and it is, therefore, highly desirable that the polymer melt having a high melt strength and a good retention of shape. Similarly, the 5 ionic copolymers of the present invention are extremely useful for the preparation of foams in that they overcome the extremely low strength of the foamed but not yet solidified polymer which has been a major problem in 10 foam extrusion and which frequently has caused the collapse of the foam.

An additional advantage that can be obtained 15 in the copolymers of the present invention is coloration. By proper choice of metal ions and combinations of metal ions many colors can be produced in the ionic copolymers. This method coloration has advantages over polymer dyeing in that dyes have a tendency to exude from hydrocarbon polymers and frequently are not compatible therewith. It also 20 has an advantage over coloration by pigmentation in that the coloration is more uniform and even, particularly in light colours. Furthermore, colored compositions can be made transparent.

The ionic copolymers may be modified, if desired, by the addition of antioxidants, stabilizers, fillers and other additives commonly employed in hydrocarbon polymer. It is generally preferred to employ additives which do not interfere with the ionic crosslinks, i.e., compounds which do not meet the requirement 30 of crosslinking compounds set forth above or if ionic in nature to employ such metal ions as would complement the metal ions used in the crosslinking. Generally, however, additives do not interfere with the ionic crosslinks since they are not of the type which would result 35 in metal ions and, furthermore, are employed in very small quantities. If desirable, the 40 copolymers of the present invention can be blended with other hydrocarbon polymers to meet particular needs of an application. In order to realize the surprising properties 45 obtained in ionic copolymers, it is essential that the ionic copolymers do not contain any significant number of covalent crosslinks, since the latter would obscure and overshadow the 50 ionic crosslinking.

The high molecular weight ionic copolymers 55 of the present invention can be extruded into films of excellent clarity, fibers of outstanding elasticity and resilience, pipes with superior stress-crack resistance, wire coatings with improved cut-through resistance and good dielectric properties despite the presence of metal ions, and foamed sheets; they can be further injection molded into intricate shapes and closely retain the dimension of the mold; 60 they can be vacuum formed, blow molded and compression molded with greater ease and better properties than linear hydrocarbon polymers. Ionic copolymers can, furthermore, be drawn and uniaxially and biaxially oriented. 65 Ionic copolymer surfaces, furthermore, are

printable and adhere well to adhesive commercially available. Thus, they can be laminated to paper, metal foil, and other plastic surfaces. The adhesion of the ionic copolymer is so good that they themselves can be employed as adhesives. Low molecular weight 70 ionic copolymers, particularly are useful for such purposes. Many other uses and modifications of the ionic copolymers of the present invention will be apparent from the foregoing 75 description and it is not intended to exclude such from the scope of this invention.

WHAT WE CLAIM IS:—

1. A copolymer characterized by having 80 ionic crosslinks in the solid state, which crosslinks are removable on fusion of the copolymer and restored on its reversion to the solid state, which comprises ethylene and an alpha, beta ethylenically-unsaturated mono- or di-carboxylic acid, the ethylene content being at least 50 moles%, and the acid monomer content being from 0.2 to 20 mole%, the copolymer having a melt index of 0.1 to 100 g/10 minutes in the absence of metallic ions and wherein at least 10% of the carboxylic acid groups are neutralized by one or more metal ions having a valence of 1 to 3 when the acid monomer is monocarboxylic, and a valence of 1 when said monomer is dicarboxylic.
2. A copolymer as claimed in claim 1, in which the ethylene content is at least 80 mole%.
3. A copolymer as claimed in claim 2 which comprises an unsaturated monocarboxylic acid 95 content of from 1 to 10 mole%.
4. A copolymer according to any of claims 1 to 3 in which the unsaturated carboxylic acid component is acrylic acid or methacrylic acid.
5. A copolymer according to any of the preceding claims in which at least 50% of the carboxylic acid groups are neutralized by the metal ions.
6. A copolymer according to any of the preceding claims which is a terpolymer and contains as the third component, units derived from a polymerizable ethylenically unsaturated ester of a monocarboxylic acid.
7. A copolymer as claimed in claim 6 in 110 which the polymerizable unsaturated ester present as the third component is vinyl acetate.
8. A copolymer according to any of the preceding claims in which the metal ions are of Group I or II of the Periodic Table of Elements.
9. A copolymer as claimed in claim 8 in which the metal ions are sodium ions.
10. A copolymer as claimed in any of the preceding claims in which the copolymer in 125 the absence of metallic ions has a melt index of from 1 to 20 g/10 minutes.
11. A copolymer as hereinbefore described in particular reference to any of the foregoing Examples.

12. A process for the preparation of the copolymers claimed in any of the preceding claims, which comprises neutralizing at least 10% of the carboxylic acid groups of a copolymer, having a melt index of 0.1 to 100 g/10 minutes, formed by the direct copolymerization of ethylene and an alpha, beta ethylenically-unsaturated carboxylic acid having one or two carboxylic acid groups, the ethylene content in said copolymer being at least 50 mole percent and the acid monomer content being from 0.2 to 25 mole percent, with one or more ionic metal compounds, the metal ion therein having a valence of 1 to 3 when the acid is monocarboxylic, and a valence of 1 when the acid is dicarboxylic.

13. A process according to claim 12 wherein the metal compound employed is an acetate, formate, hydroxide or methoxide.

14. The process substantially as set forth in any of the foregoing Examples.

15. The copolymers whenever prepared by the process hereinbefore claimed.

16. Shaped articles including fibers or films whenever obtained from the copolymers claimed in any of claims 1 to 11 and 15.

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